

Characterization of EB-PANI, ES-PANI and Copper Doped PANI

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Abstract

Three types of polyaniline varieties EB-PANI, ES-PANI and copper doped PANI have been characterized. The $\pi \rightarrow \pi^*$ transitions are clearly exhibited in solution samples of PANI. However, the absorption spectra in thin films exhibit peaks at different values, explainable as per Stafstrom's picture. The FTIR in all PANI varieties exhibit the characteristics of PANI chain. The copper linked vibrations are also seen for copper doped PANI. The X-ray spectrum are also all alike for different PANI varieties with an additional peak at a low 2θ value for copper based PANI. The changes in morphology of films of PANI varieties are seen as per SEM photographs.

Key words: Polyaniline, copper doped PANI, UV-visible spectrum, FTIR, X-ray diffraction, SEM.

Introduction

The changes in physico-chemical properties of polyaniline (PANI) under various external stimuli are used towards applications in organic - electrodes, sensors and actuators [1-3]. The other uses may be towards development of plastic micro-electronics [1,2], electrochromic devices [4], tailor-made composite systems [5,6] and smart fabrics [7]. The establishment of physical properties of PANI prepared under different conditions is thus of much importance.

Studies in Iron-doped PANI composite thin films have been reported recently[8]. Accordingly, in this work it has been found interesting to characterize samples of undoped PANI and its copper doped derivative through UV- Visible absorption, FTIR, X-ray & SEM studies.

Synthesis of PANI without metal doping

Materials used: The chemicals used for synthesis are as follows.

1. Aniline ($C_6H_5NH_2$ - Analar grade)
2. Copper sulphate ($CuSO_4.5H_2O$)
3. Hydrochloric acid (HCl)
4. Ammonium per sulphate (APS)
5. Acetone
6. Methanol.

Methodology

For this, the procedure of Mac Diarmid et al. [9] was adopted. In the experiment 0.04 mol. of APS was dissolved in 100 mL 1M HCl and the mixture was ice cooled. Then 0.04 mol. of monomer aniline was dissolved in 100 mL 1M HCl and it was also ice cooled. The ice cold APS solution was added slowly to the aniline solution with continued stirring for 30 minutes, keeping the temperature of mixture near 0°C. The polymerization was then allowed for the next 2 hours, after which the product was filtered and washed with methanol and water. The resulting mass was vacuum dried at 60°C for six hours to yield HCl-PANI or emeraldine salt (ES from of PANI). This is also the protonated form of PANI.

Synthesis of emeraldine base form of PANI

The HCl-PANI prepared as above was deprotonated by agitating it with a 1M solution of NH_4OH for six hours. The resulting product was filtered and dried in vacuum over at 60°C. This gives EB-PANI.

Synthesis of Cu^{2+} doped PANI

The above material was made by using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as the doping material. The copper sulphate was first dissolved in distilled water and this liquid was added to the basic aniline mass during synthesis of PANI with copper doping.

Preparation of PANI thin films

Various techniques are in vogue for thin film preparation viz.

- A. Electro-chemical deposition.
- B. Dip coating
- C. Spin-coating
- D. L.B. technique
- E. Layer by Layer technique
- F. Thermal evaporation
- G. Vacuum evaporation
- H. Dip-coating

In the present work, the technique of vapour deposition was used for making PANI thin films for UV-Visible absorption and SEM examination. Fig. 1 is the setup for vapour evaporation deposition. The films prepared were of ES-PANI and copper doped PANI.

UV-Visible spectrum

The UV-Visible spectrum of EB-PANI without metal doping, when dissolved in 1-methyl 2-pyrrolidene (NMP) was recorded with the reference cell containing NMP alone taking the help of a Hitachi U-3900 spectrometer Fig. 2 show the UV-visible spectrum, thus recorded from 250 nm to 800 nm for the PANI sample.

Two absorption peaks of good oscillator strengths are clearly seen in the

optical absorption spectrum at 328 nm and 635 nm. These are characteristic of emeraldine base form of PANI. It thus seems that deprotonation of salt occurs in the PANI sample before recording the spectrum for EB-PANI as well. This is in conformity with the studies of Pruneanu et al, [10] who have reported that excess of NMP leads to the deprotonation of dissolved PANI salt to the emeraldine base form due to C = O groups in NMP forming hydrogen bonds with the dopant and thus withdrawing the proton doping of PANI. It may be mentioned that no deprotonation was seen for solvents of other nature [11], such as methanol and acetonitrile.

The 328 nm band can be assigned to $\pi - \pi^*$ transition in the benzenoid ring structure [12, 13]. The absorption in the visible range, at 635 nm, is however ascribed to exciton absorption due to benzenoid to quinoid transition [14].

Finally, the highest energy shoulder peak at 268 nm may be attributed due to π to π^* charge transfer in aniline monomer [15] left over, after the polymer formation. It may be mentioned that the present optical absorption recordings were for PANI dissolved in NMP, wherein ES-PANI had got deprotonated and thus no polaron assisted peaks [16] could be observed.

Fig. 3 further shows UV-Visible spectra for EB-PANI and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ doped PANI together. It is seen that Cu PANI shows a peak at 570 nm and another at 365 nm. The peak observed at 634 nm in EB-PANI is thus blue shifted in Cu doped PANI, indicating partial oxidation of the polymer backbone [17]. An examination of UV-Visible spectrum of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as in Fig. 4 shows that copper gets well inserted in PANI system, as individual peaks of dopant are not at all seen in the absorption spectrum of Cu-PANI. Higuchi et al. [18] have also obtained similar observations, while using CuCl_2 as dopant. They further conclude that the observed spectral shift is due to complexation between the Cu^{2+} ion and PANI.

UV-Visible spectrum of ES-PANI thin films

Fig. 5 shows the UV-Visible absorption spectrum of ES -PANI thin films, recorded in the wavelength range from 300 nm to 800 nm. This spectrum is seen to be quite different from that of Fig. 4 for copper-doped PANI samples dissolved in NMP. In the spectrum of Fig. 5, well identified peaks are seen at 305 nm and 440 nm. No peaks of appreciable strength were however seen for higher wavelengths up to 800 nm. The thin film sample over the glass substrate was obviously protonated and had an expected greenish yellow shade. Stafstrom et al [16] have presented energy level calculations for highly conducting polyaniline. The typical energy levels (in atomic units) for the polaron lattice responsible for optical absorption are shown in Fig. 6.

In the Fig. 6, the levels "c" and "b" each are fully occupied in polaron lattice of PANI, whereas the level "a" is only half-filled due to 50% proton doping, leading to the withdrawal of electrons. The level "a" is thus filled only up to half height (E_F). Finally, there is a flat upper polaron band $\pi \times \pi$ which is nearly degenerate with the conduction band (x). Now the transition from band "c" to band "a" with

acquired energy of 2.6 eV gives an absorption peak at 475 nm. The absorption from band “c” to “x” and “x” involves nearly 4.1eV of energy, giving two overlapping absorptions near 301 nm. The absorption from band “c” to “a” will however involve quite variable energies from 1.8 eV to 0.9eV and thus a broad absorption in the range 686 nm to 1372 nm would be expected. The observed band positions at 305 nm and 440 nm obviously seem to support the polaron lattice hypothesis of Stafstrom et al [16]. The expected near I.R. band is however scarcely indicated in our observations as these could be made only upto 800 nm of wavelength.

Fourier Transform Infra-Red

FTIR (Fourier Transform Infra-Red) is the technique that provides information about the chemical bonding or molecular structure of materials, whether inorganic or organic. It is thus an indispensable tool for the structural characterization of conducting polymers. The frequencies and intensities of various vibrational bands exhibited by a given PANI sample thus uniquely characterize it.

In this work the FTIR spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} with a Nicolet FTIR spectrometer (model 510 P) with 4 cm^{-1} resolution. The spectra were recorded in discs made from the powderforms of PANI with KBr.

Fig. 7 shows FTIR spectrum of copper doped PANI. This curve in shows vibration bands around 3425, 1582, 1510, 1305, 1230, 1140, 770, 600 and 460 cm^{-1} . Most of these values are characteristics of PANI chain as per theoretical predictions [19]. The band at 3425 cm^{-1} is likely due to H_2O group's remnant in the KBr pellet. The peaks at 1582 cm^{-1} and 1510 cm^{-1} may be related to quinoid and benzenoid structures within PANI as $\text{C}=\text{C}$ vibrations. The 1305 cm^{-1} and 1230 cm^{-1} bands are related to $\text{C}-\text{N}$ and $\text{C}=\text{N}$ stretching modes. The 1140 cm^{-1} and 770 cm^{-1} bands are due to in plane and out of plane $\text{C}-\text{H}$ bending modes. Finally, the bands at 600 cm^{-1} and 460 cm^{-1} at lower frequencies are due to copper linked vibrations. It may be stated the ES-PANI did not show up the two lower frequency bands. The above results support the conclusions of Polk et al [20]. The FTIR spectrum of EB-PANI was, however, reported by Upadhyaya and Kakati [21] yielding peaks at 1597, 1487, 1346, 1149 and 810 cm^{-1} at close by values close by to above set of bands.

X-ray diffraction

A diffraction pattern is a distribution of scattered intensity as a function of twice the scattering angle (2θ). In the present work, X-ray diffractograms were taken for ES-PANI and copper doped PANI using $\text{K}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) on Rigaku x-ray diffractometer.

The diffractometer run for ES - PANI is shown in Fig. 8 and for copper doped PANI in Fig. 9. For ES-PANI, medium and sharp peaks are observed at 2θ values of 9.5°, 14.5°, 21.0°, 25.5°, 27.0° and 29.0°. For copper doped PANI six of seven peaks observed are as for ES-PANI. However, for

this sample an additional peak is observed at 6.4° . This shows that crystallites of some copper compound are also formed in copper doped PANI reflecting a major diffraction peak for 2θ as 6.4° .

The XRD plot for EB-PANI is, however, already reported by Upathyaya and Kakati [20]. They observed a very broad peak at $2\theta = 12^\circ$ and a low intensity peak at $2\theta = 24^\circ$. The crystalline character is thus very feeble for EB-PANI sample.

SEM studies of EB-PANI

The SEM image of EB-PANI and ES-PANI are shown in Figs. 10 (a) and 10 (b). For EB-PANI, the morphology is irregular and granular.

However, for ES-PANI aggregation of polymer chains is apparent and interchain linkages are seen. The copper doped PANI samples also exhibited a SEM pattern similar to Fig. 10(b).

Conclusions

The conclusions derived from various studies on characterization of PANI samples may be summarized as below.

(a) UV- Visible absorption

The UV Visible absorption spectra obtained, after dissolving the samples in NMP solvent, indicate that these get modified due to hydrogen bond formation with solvent molecules. The protonation in ES-PANI thus gets disappeared and observed. spectra represent only the EB-PANI form.

(b) FTIR

The FTIR characterization studies indicate similar results for all variety PANI samples. However, vibration frequencies seem to have decreases for EB-PANI compared to other variety PANI samples. In copper doped PANI, corresponding lower frequency peaks of metal linkage at 770 cm^{-1} and 460 cm^{-1} are also seen.

(c) X-ray diffraction

The x-ray studies indicate near-identical nature for all PANI samples. However, the XRD peaks are broad and dull for EB- PANI. For ES-PANI and copper doped samples, the peaks are very strong indicating long range crystalline order in these samples.

(d) SEM Studies

For EB-PANI, the morphology is irregular. However, for other two varieties interchain linkages are seen.

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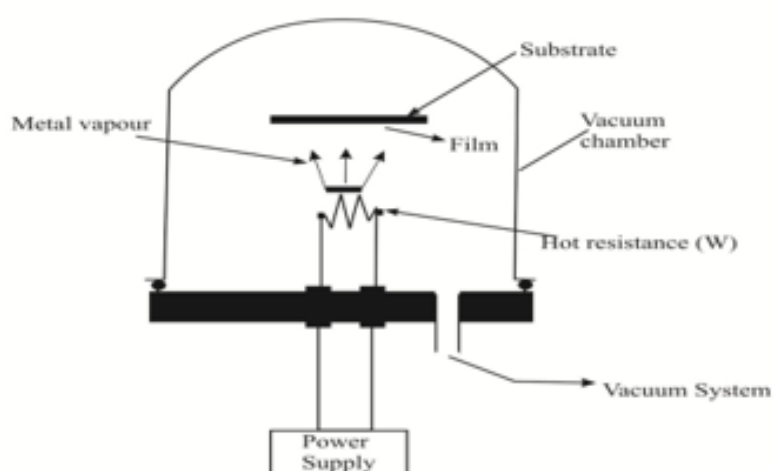


Fig. 1 Schematics of film deposition equipment.

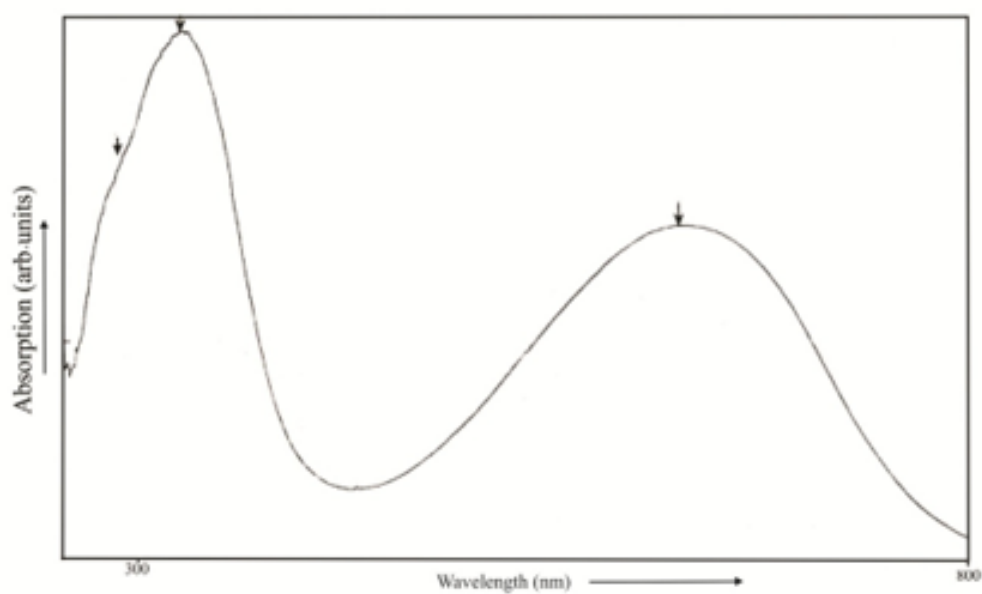


Fig. 2 UV - Visible absorption spectra of EB-PANI with cobalt doping.

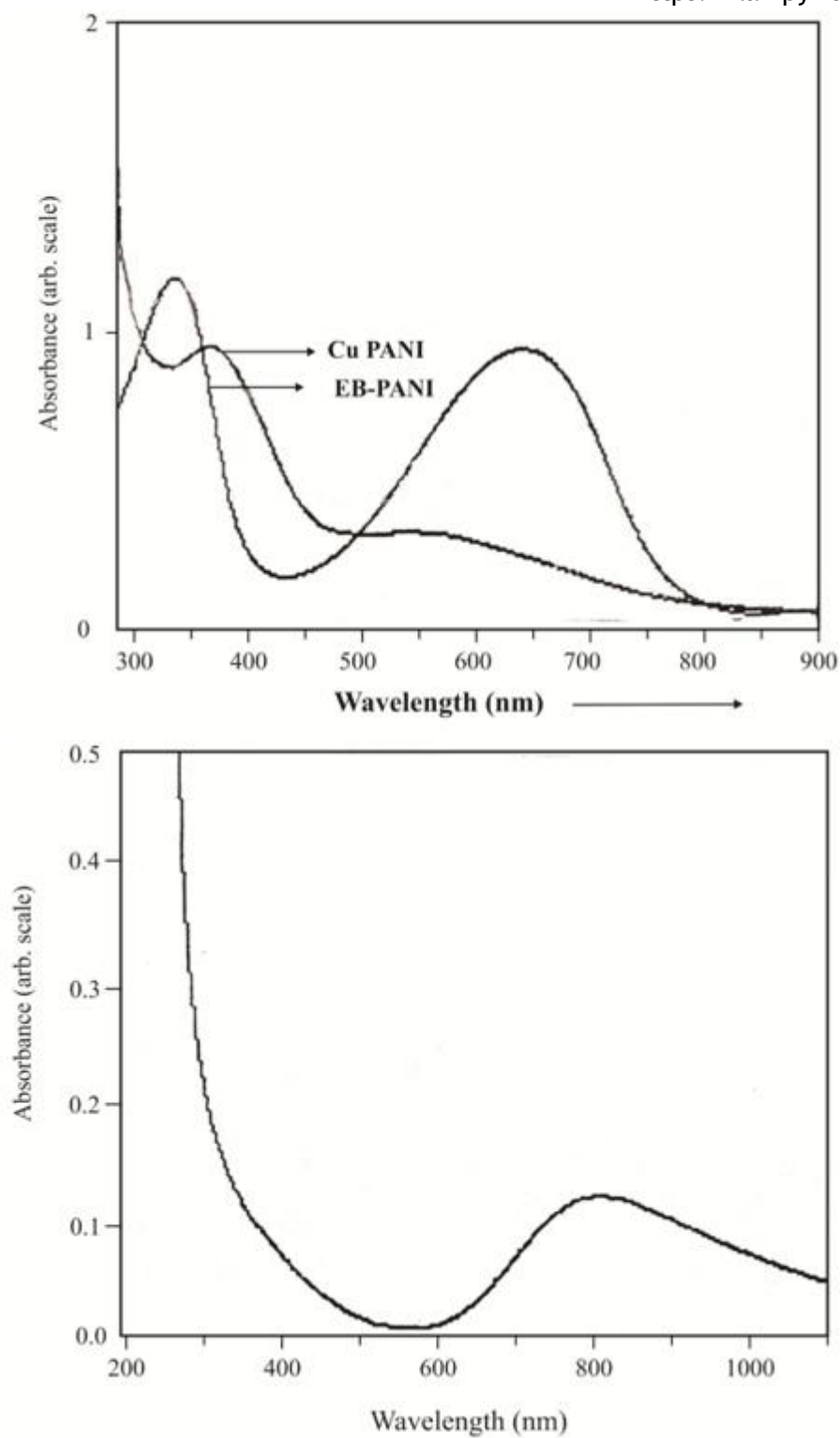


Fig. 4 UV-Visible spectrum of CuSO₄·5H₂O

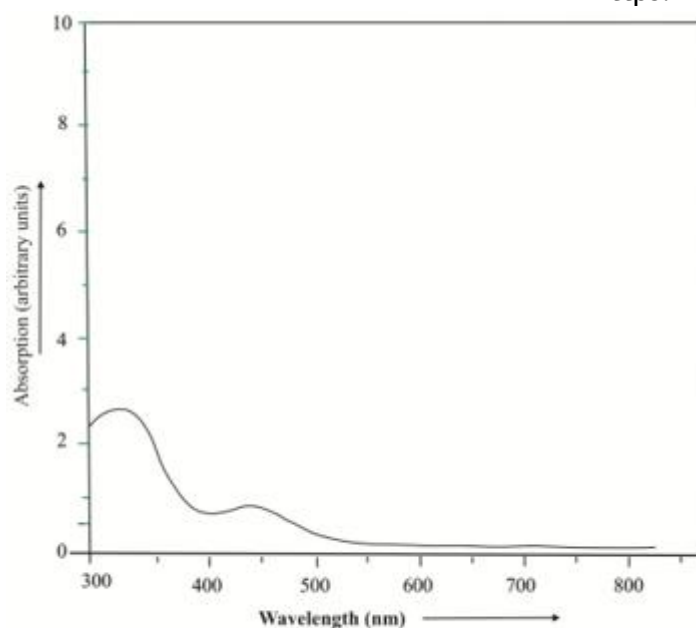


Fig. 5 UV – Visible absorption spectra of ES- PANI film (vacuum deposited).

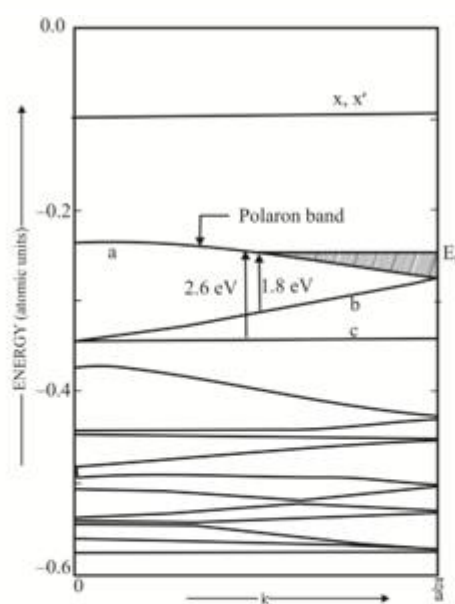


Fig.6 Band Struture for polaron lattice of 50% proton doped polyemeraldine.

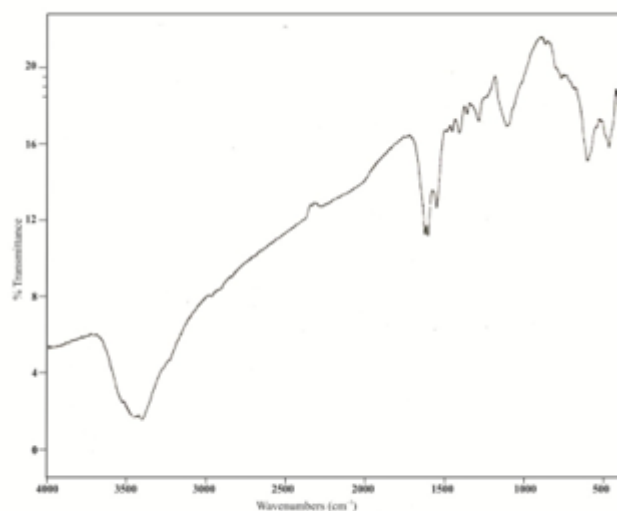


Fig. 7 FTIR spectra of PANI with cobalt doping.

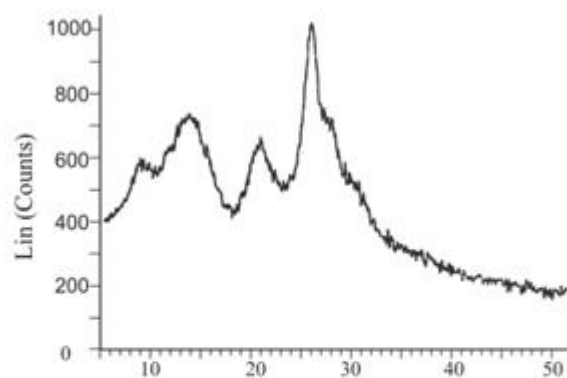


Fig. 8 X-ray diffractogram for ES-PANI without any metal doping.

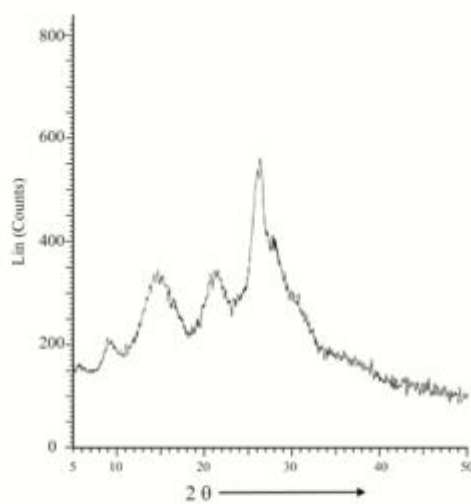


Fig. 9 X-ray diffractogram for PANI with copper doping.



Fig.10 SEM photographs of (a) EB-PANI (b) ES-PANI films.